

*Studies of the Processes Operative in Solutions. XXXI.—
Sulphonic Acids and Sulphuric Acid as Hydrolytic Agents
—a Discussion of the Constitution of Sulphuric and other
Polybasic Acids and of the Nature of Acids.*

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“Most of the phlogistian chemists admit of the existence of vital air as a component part of acids; a position which seems indeed to be as well established upon fact as any part of the science of chemistry.” ‘The First Principles of Chemistry.’ By William Nicholson, London, 1790.

Those who are conversant with the history of the development of our present theory of structure are aware that the constitution of lactic acid was the subject of discussion, in the years 1858–1860, by the distinguished German chemist Kolbe and the equally distinguished French chemist Wurtz, the latter contending that the acid was dibasic, whilst Kolbe held that it was a monatomic monobasic acid, viz. hydroxypropionic acid—a view which has long been accepted.

The discussion has an important place in chemical literature, as it practically involved the recognition of the doctrine that organic acids owe their distinctive properties to the presence of the carboxyl radicle, (CO.OH).

We propose to deal with sulphuric acid in a similar manner and to advocate the view that it is not a dibasic acid in the proper sense of the term but more nearly the inorganic equivalent of lactic acid—a view which is applicable probably not only to all “polybasic” inorganic acids and to carbonic acid but also to “hydrated” basic oxides; moreover the argument we shall advance is one which raises wide issues as to the properties and structure of “salts” generally.

Sulphuric acid has been constantly under consideration by one of us since 1870; indeed, the present memoir may be regarded as Part II of a communication made to this Society, in that year (the subject of his thesis for the Ph.D. degree in Leipzig), entitled “Contributions to the History of the Acids of the Sulphur Series.”* It may be added that a communication which he made to the Chemical Society in the following year†—“On the Formation of Sulpho-acids”—actually opens with the statement “Occupied

* ‘Roy. Soc. Proc.’ vol. 18, p. 502 (1870).

† ‘Chem. Soc. Journ.’ 1871, p. 173; ‘B.A. Report,’ 1885, p. 961.

with an investigation into the constitution of sulphuric acid, the views on which are, as is well known, extremely conflicting, etc." Throughout the interval, he has never ceased to pay attention to the acids of the sulphur series. Of late years, however, the subject appears to have lost interest, on the theoretical side, in the minds of most chemists, as the habit of writing formulæ in accordance with the fashion which set in at about the time referred to has exercised so great an influence that it has been generally assumed that the problem was solved in favour of the symmetrical formula $\text{SO}_2(\text{OH})_2$, which has long been used, without question, as representative of sulphuric acid.

In point of fact, the problem was scarcely ripe for solution: considerations such as can now be advanced were not then available; indeed the conception of "an acid" was still a vague one—and it is far from definite yet, notwithstanding the fundamental importance of acids.

It must not be forgotten that hitherto we have had no decisive methods of deciphering constitution in the case of the simpler compounds, especially those of elements other than carbon. In the case of carbon, the number of compounds is so immense that it has been possible to put our chemical hypotheses to the test of practice over and over again and the odds are so enormously in favour of our fundamental postulates that we may claim to have devised a symbolic system which is self-contained and a practically complete expression of the facts: whatever change may take place in our views of structure, whatever the extent to which they are modified in course of time, our present symbolic language is so complete that it will only be necessary, probably, to translate its terms into those of the new tongue. But in the case of elements other than carbon, it has not been possible to ring the changes in such a way as to favour one particular view to a preponderating extent: fortunately, new methods are now being developed and, it may be hoped—in view of the remarkable results arrived at by Barlow and Pope, by Laue and by the Braggs, correlating crystalline form with internal structure—that ere long we shall be able to deal even with "simple" substances.

In discussing the nature of acids and the manner in which they act, it is all important to remember the conception embodied in the word oxygen and why it is that one of the gases in air was so named originally: the argument is best stated in Lavoisier's own words:—*

"Nous avons donné à la base de la portion respirable de l'air le nom d'oxygène, en le dérivant de deux mots grecs, *ὀξύς*, *acide*, *γεννῶμαι*, *j'engendre*, parce qu'en effet une des

* 'Traité élémentaire de Chimie.' See 'Œuvres de Lavoisier,' Tome I, Paris, 1864.

propriétés les plus générales de cette base est de former des acides en se combinant avec la plupart des substances. Nous appellerons donc gaz oxygène la réunion de cette base avec le calorique."

The highest oxides of phosphorus, sulphur and carbon were named by Lavoisier phosphoric, sulphuric and carbonic acid respectively.

His prescience was remarkable. No more significant term has ever been devised, as it is undeniable that oxygen *is* the acidifying principle, *par excellence*, whether or no all acids contain oxygen: though many oxides are basic substances, the metals in them being sufficiently positive to overmaster the negative properties of the oxygen, it is true generally that the more highly oxygenated they are, the less they are basic and that, in not a few cases, the addition of oxygen to basic oxides involves ultimately their conversion into acidic oxides.

The distinction between acid, base and salt was made very clearly by Lavoisier in the following passage:—

"Les substances acidifiables, en se combinant avec l'oxygène et en se convertissant en acides, acquièrent une grande tendance à la combinaison; elles deviennent susceptibles de s'unir avec des substances terreuses et métalliques et c'est de cette réunion que résultent les sels neutres. Les acides peuvent donc être regardés comme de véritables principes salifiants et les substances auxquelles ils s'unissent pour former des sels neutres comme des bases salifiables."

That the bases were less well understood in his day than the acids is obvious:—

"On ne connaît pas mieux, jusqu'ici, les principes constituants de la soude que ceux de la potasse et on n'est pas même certain si cette substance est toute formée dans les végétaux antérieurement à la combustion. L'analogie pourrait porter à croire que l'azote est un des principes constituants des alcalis en général et on en a la preuve à l'égard de l'ammoniaque, comme je vais l'exposer; mais on n'a, relativement à la potasse et à la soude, que de légères présomptions qu'aucune expérience décisive n'a encore confirmées."

But none the less Lavoisier had very clear perceptions of the nature of the process by which salts are formed even from metals—

"Mais il faut observer que les alcalis et les terres entrent purement et simplement dans la composition des sels neutres sans aucun intermède qui serve à les unir; tandis qu'au contraire les métaux ne peuvent se combiner avec les acides qu'autant qu'ils ont été préalablement plus ou moins oxygénés. On peut donc rigoureusement dire que les métaux ne sont point dissolubles dans les acides mais seulement les oxydes métalliques. Ainsi, lorsqu'on met une substance métallique dans une acide, la première condition pour qu'elle puisse s'y dissoudre est qu'elle puisse s'y oxyder et elle ne le peut qu'en enlevant de l'oxygène ou à l'acide ou à l'eau dont cet acide est étendu: c'est-à-dire, en d'autres termes, qu'une substance métallique ne peut se dissoudre dans une acide qu'autant que l'oxygène qui entre, soit dans la composition de l'eau, soit dans celle de l'acide, a plus d'affinité avec le métal qu'il n'en a avec l'hydrogène ou la base acidifiable: ou, ce qui revient encore au même, qu'il n'y a de dissolution métallique qu'autant qu'il y a décomposition de l'eau ou de l'acide."

And Lavoisier also had a shrewd suspicion of the nature of bases such as lime, magnesia, baryta and alumina, thus:—

“L’oxygène est donc le moyen d’union entre les métaux et les acides : et cette circonstance, qui a lieu pour tous les métaux comme pour tous les acides, pourrait porter à croire que toutes les substances qui ont une grande affinité avec les acides contiennent de l’oxygène. Il est donc assez probable que les quatre terres salifiables que nous avons désignées ci-dessus contiennent de l’oxygène et que c’est par ce *latus* qu’elles s’unissent aux acides. Cette considération semblerait appuyer ce que j’ai précédemment avancé à l’article des terres, que ces substances pourraient bien n’être autre chose que des métaux oxydés, avec lesquels l’oxygène a plus d’affinité qu’il n’en a avec le charbon et qui, par cette circonstance, sont irréductibles. Au reste ce n’est ici qu’une conjecture que des expériences ultérieures pourront seules ou confirmer ou détruire.”

The accuracy of this last deduction, it is well known, was established by Humphry Davy in his communications to this Society in 1807–1809.

After the introduction of the atomic theory, salts were always formulated as binary compounds formed by the union of two oxides—the acid and the base. The celebrated dualistic hypothesis advocated by Berzelius merely involved the additional assumption that the acid and the base were held together in virtue of their opposite electrical charges—a conception which was developed later on by Faraday and finally by Helmholtz into the hypothesis of charged atoms and ions, the root-conception of the electrolytic dissociation hypothesis introduced by Clausius and afterwards extended by Arrhenius.

The modern conception of an acid was of slow growth. The view advanced by Lavoisier, that oxygen was the acidifying principle, suffered eclipse when Davy published his celebrated proof that “spirit of salt” was not an oxygen compound but simply a compound of hydrogen with the element chlorine.

On this account and because of the “acidic” properties of sulphuretted hydrogen and of hydrogen cyanide, it became customary to recognise two classes of acids—*hydracids* (such as hydrogen chloride) and *oxyacids*. Davy even went so far, in 1815, as to suggest that hydrogen was the characteristic constituent of all acids. Later on, the acids were classed as hydrogen salts, mainly in consequence of Graham’s investigation of the phosphates communicated to this Society in 1833. Graham, it is well known, came to the conclusion that phosphoric acid, P_2O_5 , combined with the base water in three different proportions to form three different *phosphates of water*: in like manner, he applied the term *sulphate of water* to the compound $H_2SO_4 = SO_3.OH_2$.

But the oxides SO_3 and P_2O_5 were long spoken of as acids and the compound SO_4H_2 was commonly termed the monohydrate of sulphuric acid, briefly *monohydrate*, by makers and users of the acid. Gradually, however, the term acidic oxide or anhydride was substituted for that of acid in the

case of such oxides; but even at the present day carbonic acid remains the popular name of carbon dioxide, so that we still have one link with the past.

The issue has been further complicated by the introduction of the ionic dissociation hypothesis. According to this, substances such as those represented by the formulæ HCl , HNO_3 and H_2SO_4 undergo "dissociation" when dissolved in water and the constituent common to and characteristic of all acid solutions is the free hydrogen ion: the strength of an acid, it is assumed, depends on the extent to which it thus undergoes dissociation, so that the effective acidity of weak solutions of an acid is commonly spoken of in terms of the concentration of the hydrogen ions. It is not legitimate, therefore, to speak of compounds such as those referred to as acids: nevertheless this is still done. In 1885, prior to the popularisation of the Arrhenius hypothesis, one of us insisted that hydrogen chloride was not an acid substance in itself and that it acted as an acid only when in conjunction with water:* the proposition was then made and has since been often repeated that the term acid should be confined to the solution: the term *chlorhydric acid* was advocated as a suitable name for the complex conceived to be present in the solution. The meaning Lavoisier attached to the term acid would be restored if this view were adopted and applied generally: all acids would contain oxygen (or an equivalent element in the periodic series) and the acid function would be one conditioned by the presence of oxygen—though not of oxygen alone but of oxygen in association with hydrogen, "acidification" being the consequence of the addition of hydrone.

Having thus directed attention to one of the main issues we desire to raise, we now pass to the consideration of the properties of sulphuric acid.

The Properties of Sulphuric Acid.

These are peculiar in many ways. The anhydride exists in two forms: one of these apparently has twice the molecular weight of the other: in this connexion, it is noteworthy that the complex acid chloride $\text{S}_2\text{O}_5\text{Cl}_2$ derived from two molecules of the anhydride, not the simple chloride SO_2Cl_2 derived from a single molecule, is formed by the direct interaction of sulphuric anhydride and carbon tetrachloride as well as in several other similar interactions.

Sulphuric anhydride combines readily not only with hydrogen chloride but also with methylic and ethylic chlorides.

When sulphuric acid is subjected to the action of phosphorus pentachloride, the compound produced, SO_3HCl , is identical with that formed by associating the anhydride with hydrogen chloride: on further treatment with the

* 'Brit. Assoc. Report,' Aberdeen, 1885, p. 960.

pentachloride, however, the compound which is formed is the complex chloride $\text{S}_2\text{O}_5\text{Cl}_2$, not the simple chloride SO_2Cl_2 .

This latter compound is obtained by combining sulphur dioxide directly with chlorine. It is a remarkable fact that both the anhydro-chlorides, SO_2Cl_2 and $\text{S}_2\text{O}_5\text{Cl}_2$, are powerful *chlorinating* agents.

On the other hand, the anhydride and both the compounds SO_3HCl and $\text{S}_2\text{O}_5\text{Cl}_2$ are powerful *sulphonating* agents.

Sulphuric acid is commonly regarded as *dibasic*, because it forms both acid and normal sulphates such as are represented by the formulæ NaHSO_4 and Na_2SO_4 : but no valid proof of the molecular weight of these salts has been given; hence it is open to us to regard the acid salts as formed either by the displacement of half the hydrogen in a "molecule" of the acid or by the association of a "molecule" of the acid with a "molecule" of the normal or neutral salt.

It is remarkable, that although sulphuric acid is the strongest of acids, the "strength" of the acid, deduced from the molecular electrical conductivity of moderately dilute solutions, is less than 20 per cent. greater than that of chlorhydric and nitric acids: *at high dilutions*, however, the value rises to about double that of the strong monobasic acids.

The molecular hydrolytic activity of sulphuric acid is also greater, though only to the extent of nearly 20 per cent., than that of chlorhydric and nitric acids. But the acid ethereal salts of sulphuric acid and the sulphonic acids are strong monobasic acids only very slightly inferior in strength to chlorhydric and nitric. This perhaps is the most striking fact to be taken into account in considering the structure of the acid.

It appeared to us that a further study of the sulphonic acids as hydrolytic agents was desirable, in view of the small amount of information extant, especially as they have not been studied hitherto at comparative concentrations nor more than superficially and no attention has been paid to the polysulphonic compounds.

It is well known that the properties of benzene itself are greatly modified by the introduction of what may be termed neutral radicles. The homologous hydrocarbons formed by methylating benzene are all more "active" substances than the parent hydrocarbon: but when halogens or negative compound-radicles such as NO_2 are introduced into benzene its "activity" is reduced. The benzene system, therefore, appears to be a plastic system capable of responding to each and every change that is made in its composition.

When either of the radicles OH and NH_2 is introduced into benzene, the activity rises; but by introducing hydrocarbon or acid radicles in place of the hydrogen into either of the groups, the influence these radicles exercise

on benzene is altogether modified and reduced: and not only is this the case but there is reason to believe that the oxygen and nitrogen atoms themselves are also modified by such treatment and rendered less receptive. In other words, there is evidence that both the benzene complex and compound radicles such as OH and NH_2 are "plastic" systems and that they are reciprocally affected, when in association, by changes made in either system.

The benzene system is also modified by sulphonation: little is known, however, as to the way in which the sulphonic radicle, SO_3H , is affected by association with a hydrocarbon radicle or by changes made in the hydrocarbon radicle to which it is attached: whereas, in the case of carboxylic acids, the strength of the acid is increased by the introduction of negative elements into the radicle with which it is combined, the few cases studied hitherto appear to show that the strength of the sulphonic acids is lowered. Experiments carried out by one of us have shown, however, that modifications so "distant" as those affected by altering the OH group in phenol-parasulphonic acid, $\text{HO.C}_6\text{H}_4.\text{SO}_3\text{H}$, by introducing methyl in place of the hydrogen atom in the hydroxyl group, may modify the properties of the SO_3H radicle—consequently, it would seem that even when three compound systems are associated in a single molecule all are reciprocally affected by a change made in any one of the three.

The Hydrolytic Activity of Sulphonic Acids.

The following acids have been used by us:—

- I. Benzenesulphonic acid, $\text{C}_6\text{H}_5.\text{SO}_3\text{H}$: tolueneparasulphonic acid, $\text{CH}_3.\text{C}_6\text{H}_4.\text{SO}_3\text{H}$: mesitylenesulphonic acid, $1:3:5(\text{CH}_3)_3.\text{C}_6\text{H}_2.\text{SO}_3\text{H}$.
- II. Parachloro-, parabromo- and pariodobenzenesulphonic acid.
- III. Paradichloro-, paradibromo- and paradiiodobenzenesulphonic acid.
- IV. α -Bromocamphor- β -sulphonic acid.
- V. Benzeneortho-, para- and metadisulphonic acid.
- VI. Benzene-1:3:5-trisulphonic acid: toluene-1:3:5 trisulphonic acid.

The experiments were all carried out at $25^\circ \text{C.} \pm 0.01^\circ$ with the apparatus described in parts XII and XXII of this series.* The acid was weighed out in one of the flasks of the mixing apparatus and the sugar and the remainder of the water required to give the desired dilution in the other: before adding the one to the other, each solution was brought to the experimental temperature: the two liquids were then rapidly mixed and the mixture at once transferred to the polarimeter tube, which was already in position and at

* XII, 'Chem. Soc. Trans.,' 1911, p. 349; XXII, 'Roy. Soc. Proc.,' A, vol. 87, p. 539 (1912).

25° C. The amount of sugar used was always small, usually in the proportion of one-quarter of a molecular proportion to one of acid and 50 to 200 of the fundamental molecules of water: in the case of more concentrated solutions one-eighth was frequently used either instead of or as a check on the experiments with one-quarter of a molecular proportion. As in the previous inquiry, the source of light was the "mercury green" light ($\lambda = 5461$) given by a silica mercury lamp.

The final results of all the experiments made are given in Table I. Tables II to VI and VIII contain the full data of the experiments in certain representative cases: as the course of change in other cases was precisely similar and always regular, it is unnecessary to give the details of the experiments, nearly 80 in all.

The velocity coefficient K' is $10^5 K \log e$ in the equation of mass action $dx/dt = K(a-x)$ and is deduced by means of the equation (see these Studies, No. XII)

$$K' = \frac{1}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2} \times 10^5,$$

a being the initial concentration of the cane sugar and x_1, x_2 the amount hydrolysed at times t_1, t_2 , etc. The differences between the rotations R_1, R_2 at times t_1 and t_2 and the final rotations R_∞ are proportional to the concentrations $(a-x_1)$ and $(a-x_2)$ of the sugar left unhydrolysed at those times.

In the tables, the values of K' , to the nearest whole number usually, are placed opposite the values of the rotations corresponding to the times t_1 : as the interval $t_2 - t_1$ is indicated, it can be seen, therefore, which values of $(a-x)$ were used in the calculation of the constant. The times of observation were varied according to the conditions of the experiments. In cases in which hydrolysis took place very rapidly, mean readings were recorded at every 5' interval, each being the mean of 5 readings taken at the given time, at 1' and 0.5' before and at 0.5' and 1' after. When hydrolysis was effected slowly, several readings were taken at intervals close together: another set of readings was taken after a long interval of say 60' and then another similar series after another long interval. These long intervals are used as the $t_2 - t_1$ intervals. The different values of K' recorded are all deduced from different readings and have thus no common error; they refer also to consecutive portions of the interactions and generally do not overlap.

Table I.—Molecular Hydrolytic Activity (K) of Sulphonic Acids at Different Dilutions.

Acid : " water " ratio A : OH ₂	
Sulphuric acid	30 1380 40 867 50 624 60 487 80 335 100 256 150 117 200 500 1000
Benzenesulphonic acid	1067 713 525 413 287 220 98.9
Benzeneorthodisulphonic acid	1157 452 273 195
Benzeneparadisulphonic acid	522 215.3
Benzenemetadisulphonic acid	1403 734 533 312 220
1:3:5 Benzene-trisulphonic acid	982 365.5
Chlorobenzeneparasulphonic acid	499 216 97.7
Bromobenzeneparasulphonic acid	481 208 95.2
Iodobenzeneparasulphonic acid	489 214 97.4
Paradichlorobenzene-sulphonic acid	475 209 96.9
Paradibromobenzene-sulphonic acid	484 389 276 212 97.8
Paradiiodobenzene-sulphonic acid	293 223 101.3
Tolueneparasulphonic acid	1000 677 507 402 283 217.4 98.7 37 18
1:3:5 Toluenetri-sulphonic acid	950 361
Mesitylenesulphonic acid	439 203 92.7
α -Bromocamphor- β -sulphonic acid	201.3 94.3

Table II.—Benzenesulphonic Acid.

$C_6H_5SO_3H : 100 H_2O : 0.25 C_{12}H_{22}O_{11}$			
Times of observation	Observed rotation, R	$R - R_\infty$ ($\alpha - x$)	K' $t_2 - t_1 = 60'$
h. m. s.	°	°	
2 30	11.586	15.740	219
32 30	.382	.536	219
35	.204	.358	220
3 0	9.376	13.530	219
2 30	.204	.358	220
5	.032	.186	219
3 30	7.476	11.630	220
32 30	.320	.474	220
35	.170	.324	221
4 0	5.842	9.996	
2 30	.708	.862	
5	.592	.746	
4 30	4.424	8.578	
32 30	.316	.470	
35	.204	.358	
Final rotation R_∞	-4.154		Mean 219.7

Table III.—Tolueneparasulphonic Acid.

$CH_3.C_6H_4.SO_3H : 100H_2O : 0.25C_{12}H_{22}O_{11}$			
Times of observation	Observed rotation, R	$R - R_\infty$ ($\alpha - x$)	K'
h. m. s.	°	°	
1 10	11.600	15.711	218
12 30	.398	.509	217
15	.202	.313	217
17 30	.014	.125	217
20	10.826	14.937	217
1 50	8.744	12.855	217
52 30	.584	.695	217
55	.428	.539	217
57 30	.728	.389	218
2 0	.116	.227	217
3 0	4.956	9.067	
2 30	.836	8.947	
5	.722	.833	
7 30	.612	.723	
10	.500	.611	
Final rotation R_∞	-4.111		Mean 217.4

Table IV.—Mesitylenesulphonic Acid.

$(\text{CH}_3)_3\text{C}_6\text{H}_2\cdot\text{SO}_3\text{H} : 100\text{H}_2\text{O} : 0\cdot25\text{C}_{12}\text{H}_{22}\text{O}_{11}$			$(\text{CH}_3)_3\text{C}_6\text{H}_2\cdot\text{SO}_3\text{H} : 200\text{H}_2\text{O} : 0\cdot5\text{C}_{12}\text{H}_{22}\text{O}_{11}$		
Times of observation	Observed rotation, R	K'	Times of observation	Observed rotation, R	K' $t_2 - t_1 = 240$
h. m. s.	°		h. m. s.	°	
2 45	11·790	202	1 0	12·620	
47 30	·608	202	2 30	·530	
50	·432	201	5	·442	
52 30	·252	200	7 30	·348	
55	·068	202	10	·252	93·1
		$t_2 - t_1 = 75'$		12 30	93·1
			15	·076	92·8
4 0	7·118	204			92·6
2 30	6·996	204			92·5
5	·886	204	5 0	5·878	92·5
7 30	·736	203	2 30	·822	92·5
10	·606	202	5	·784	92·4
		$t_2 - t_1 = 120'$		7 30	·738
6 0	2·296		10	·690	
2 30	·234		12 30	·636	
5	·160		15	·588	
7 30	·100				
10	·034				
Final R_∞	-4·075	Mean 202·5	R_∞	-4·150	Mean 92·7

Table V.—1 : 3 : 5 Benzenetrisulphonic Acid.

$\text{C}_6\text{H}_3(\text{SO}_3\text{H})_3 : 100\text{H}_2\text{O} : 0\cdot25\text{C}_{12}\text{H}_{22}\text{O}_{11}$		
Times of observation	Observed rotation, R	K' $t_2 - t_1 = 30'$
h. m.	°	
5 0	9·434	979
5	7·978	981
10	6·670	983
15	5·502	984
20	4·456	977
25	3·520	983
30	2·684	984
35	1·932	
40	1·260	
45	0·666	
50	0·146	
55	-0·336	
6 0	-0·764	
Final R_∞	-4·304	Mean 982

Table VI.— $C_6H_4(SO_3H)_2 : 100 OH_2 : 0.25 C_{12}H_{22}O_{11}$.

Benzeneometadisulphonic Acid. Benzeneparadisulphonic Acid. Benzeneorthodisulphonic Acid.

Times of observation		Observed rotation, R	K'	Times of observation		Observed rotation, R	K	Times of observation		Observed rotation, R	K	Times of observation		Observed rotation, R	K'
h.	m.	°		h.	m.	°		h.	m.	°		h.	m.	°	
2	25	7.664	529.7	12	15	8.478	522	2	45	10.020	449	2	45	10.020	449
30		.012	533	20		7.754	521	50		9.304	453	50		9.304	453
35		6.356	535	25		.102	525	55		8.618	452	55		8.618	452
40		5.728	534	30		6.436	522	0		7.964	452	0		7.964	452
3	5	3.240	532	12	55	3.794	517	3	25	5.196	453	3	25	5.196	453
10		2.816	535	1	0	.360	524	30		4.692	452	30		4.692	452
15		.404	534	5		2.928	522	35		.248	452	35		.248	452
20		.024	532	10		.530	524	40		3.818	453	40		3.818	453
4	5	-0.424	533	1	55	-0.078		4	25	0.818		4	25	0.818	
10		.644		2	0	.322		30		.558		30		.558	
15		.832		5		.522		35		.316		35		.316	
20		-1.008		10		.726		40		.086		40		.086	
5	10	-2.288													
Final R _∞		-3.800	Mean 533	Final R _∞		-3.790	Mean 522	Final R _∞		-4.210	Mean 452	Final R _∞		-4.210	Mean 452

Discussion of the Results.

Order of the Interaction.—A point of interest, to which attention may be directed in the first place, is the fact that the rate at which the action proceeds in all cases is strictly that of a so-called unimolecular change, not only in the case of the monosulphonic acid but also in the case of each of the di- and of each of the tri-sulphonic acids.

Whatever the explanation may be of the changes involved in the phenomena of hydrolysis, it is to be supposed that the rate at which the interactions proceed under the influence of a polysulphonic acid will be that at which "unimolecular" changes are effected so long as each effective acidic centre acts independently; the results we have obtained are, therefore, proof that although the interaction involves one molecule of acid and either two or three of sugar, as the case may be, the sugar molecules are attacked separately, so that the "basicity" of the acid is in no way disclosed (*cp.* XXII, p. 570).

The molecule of a polysulphonic acid is to be pictured, in fact, as capable of acting simultaneously on as many separate, independent molecules of sugar as it contains sulphonic radicles, so that the activity of the disulphonic acid is to be thought of as exercised from a single centre equally in two directions and that of the trisulphonic acid as exercised equally in three directions.

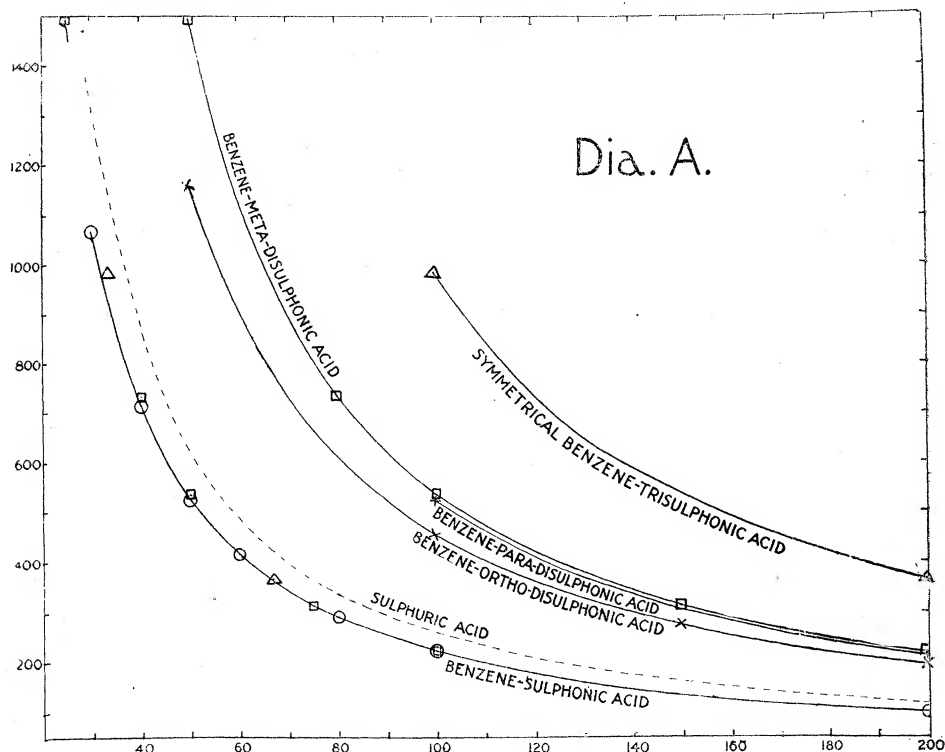
Strength of the Acids.—The benzenepolysulphonic acids are all of extraordinary strength, the metadisulphonic acid being molecularly more than twice and the trisulphonic acid more than thrice as strong as the monosulphonic acid and all but four times as strong as sulphuric acid at the concentration $A : 100H_2O$.*

If, however, the concentration of benzenemetadisulphonic acid and of benzenemetatrisulphonic acid be expressed in terms of equivalents instead of in molecular proportions, the activities of the mono-, di- and tri-sulphonic acids are the same at *equivalent* strengths. On reference to Diagram A, it will be seen that the values of the three acids all fall on one curve (that of benzenesulphonic acid). In other words, the sulphonic unit (SO_3H) has the same value in each of the three acids when the amount of water used in proportion to each unit is the same.

The explanation of the fact that the molecular activity of the disulphonic is more than twice, that of the trisulphonic acid so much more than thrice, that of the monosulphonic acid at corresponding concentrations is that each SO_3H group has a large concentrating or—to use the term adopted by recent

* In view of this result, it is conceivable that the extreme activity of some enzymes, invertase, for example, is in part due to the existence of several active centres at the surface of the colloid complex, not merely to the weakness of the specific hydrolyte with which alone it is compatible.

workers—salt effect: the amount of “free” water present in the case of the di- and trisulphonic acids is, therefore, very much less than in the case of the



monosulphonic acid when the same amount is used per molecule in dissolving the acid.

If the concentrating or “salt” effect of the acid be expressed as the “apparent hydration value,” in the manner adopted in previous communications of this series, the values obtained in the case of benzenemeta-disulphonic acid are much greater than those assigned to the monosulphonic acid and approach to twice their magnitude at the higher dilution (see Table VII).

Too much importance should not be attached to the actual numbers in this Table, as a very small error in the velocity coefficients used in deducing the values makes a large difference in the apparent hydration values; it is clear, however, that the values are much greater in the case of the disulphonic acid.

Influence of Constitution on the Strength of the Acid.—The paradisulphonic acid is slightly and the orthodisulphonic acid considerably weaker than the metadisulphonic acid. This result is one of some significance. It has long been recognised that if two radicles are present in the para-position in benzene

Table VII.

Total H ₂ O.	Apparent hydration values.	
	Monosulphonic acid.	Metadisulphonic acid.
30	9.2	—
40	11.2	—
50	12.8	18.4
60	13.6	21.0
70	14.4	23.2
80	15.0	25.3
90	15.5	27.0
100	16.0	28.0

they mutually influence each other and that this is still more the case when they are present in the ortho-position; whilst radicles relatively in the meta-position have little or no influence upon one another. Apart from any such mutual influence, the very considerable lowering in activity manifest in the case of the ortho-acid, however, may also be due to the fact that, in the case of this acid, the separate activities of the two sulphonic radicles cannot be so freely exercised as in the case of the other acids because of their proximity and the consequent difficulty the sugar molecules have in "crowding in" upon them.

The influence of halogens appears to be remarkably slight and out of all proportion small in comparison with that which they exercise in the case of carboxylic acids. Probably this is a result of considerable significance. The order in which the three halogens exercise an influence is not the same, however, in the mono- and di-substituted derivatives; in the case of the former, the activity is very slightly below that of the unsubstituted acid and bromine has the greatest influence in depressing the strength;* in the case of the latter, chlorine and bromine both depress the strength whilst iodine raises it slightly.

The influence of methyl, as shown in tolueneparasulphonic acid and still

* The experiments at the dilution A : 50 H₂O were repeated in the case of the chloro- and bromo-acids but the values of the velocity coefficients obtained were the same as previously, viz. 499 and 481 respectively. A sample of the chloro-acid was then prepared from the sulphochloride and on carrying out an experiment at the dilution A : 100 H₂O the value first obtained was confirmed. No explanation of the irregular order of the activities of the three acids can be given at present: it would appear, however, that the order observed is the correct one, as crystallographic measurements of the sulphochlorides of the three acids, which Mr. Mummery has made, show that the α -axis has a lower value in the bromo- than in either the chloro- or the iodosulphochloride, which are practically identical in their dimensions.

more in mesitylenesulphonic acid, is depressant.* Methyl has a similar influence in the case of the trisulphonic acid. It is a striking fact that bromocamphorsulphonic acid falls very little short of benzenesulphonic acid in strength.

Taking the results generally into account, it is clear that the strength of the sulphonic radicle is affected only to a relatively slight extent when alterations are made in the hydrocarbon radicle to which it is attached; but that it is subject to some modification, there can be no doubt, in view not only of the differences in strength that are manifest but also of other differences such as solubility; thus paradibromobenzenesulphonic acid is relatively slightly soluble and crystallises with extreme facility in comparison with the unsubstituted acid.

Variation in Strength on Dilution.—It will be noticed that as dilution proceeds the acids tend to behave more and more alike; it is therefore probable that the values per unit of SO_3H would not be very different at sufficiently low dilutions. The change is doubtless in part due to the gradual disappearance of the "concentrating or salt effect," already referred to, which the acid exercises in the more concentrated solutions; it may be also in part due to gradual depolymerisation of more complex molecules: such differences, between the various acids, however, could only be the outcome of constitutional peculiarities of the fundamental molecules and may therefore be regarded as an indication that the sulphonic radicle is more or less responsive to variation in the radicle with which it is associated.

An experiment was carried out, which is recorded in Table VIII, in which equal molecular proportions of benzenesulphonic acid and of toluenepara-sulphonic acid were used as the hydrolyst, the assumption being made that, in the event of each acid existing in solution as a polymerised molecule, the two acids might mutually interfere and each molecule be to some extent depolymerised: in this case, it was to be expected that the strength of each acid would be more or less raised and the strength of the mixture in excess of the calculated mean.

The result shows that the effect produced by the mixture is exactly the mean of the effects produced by the two acids separately.

This result, however, cannot be regarded as final proof that the acids are not present in a polymerised state, unless it be assumed that the molecules of the two acids are sufficiently incompatible to be incapable of associating together. As there is reason to suppose that, in some cases at least, the

* We are inclined to regard the value arrived at in the case of mesitylenesulphonic acid at a dilution of 200 as too low.

Table VIII.— $40\text{H}_2\text{O} : (\frac{1}{2}\text{C}_6\text{H}_5\cdot\text{SO}_3\text{H} + \frac{1}{2}\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}) : 0\cdot25\text{C}_{12}\text{H}_{22}\text{O}_{11}$.

Times of observation			Observed rotation, R	K' $t_2 - t_1 = 50'$
h.	m.	s.	°	
11	40		16·788	695·8
	42	30	15·756	696·3
	45		14·736	696·1
	47	30	13·776	695·8
	50		12·856	696·4
	52	30	11·974	697·1
	55		11·121	697·8
				Mean 696·5
12	30		2·094	
	32	30	1·626	$\text{C}_6\text{H}_5\cdot\text{SO}_3\text{H}$ 715·6
	35		1·170	$\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ 677·2
	37	30	0·744	
	40		0·324	Mean 696·4
	42	30	−0·080	
	45		−0·470	
Final R _∞			−9·87	

molecules of a benzenesulphonic acid form triplets* and that two isomorphous acids might well crystallise together, this assumption cannot at present be made with any degree of certainty. It will be desirable to carry out similar experiments with a mixture of incompatible acids—perhaps one of benzenesulphonic acid with a camphorsulphonic acid would satisfy this condition.

Comparison of Sulphonic with Carboxylic Acids.—The similarity in behaviour of the various acids we have examined, the almost constant “strength” of the sulphonic radicle, is in striking contrast with the inconstancy of behaviour which is manifest in the case of carboxylic acids.

The difference is well brought out in the following table of velocity coefficients originally given by Ostwald in 1883 as representing the hydrolytic activity of various carboxylic acids in volume normal solutions determined by means of methylic acetate:—

Chlorhydric acid		100·000
Formic	„	1·310
Acetic	„	0·345
Propionic	„	0·304
Butyric	„	0·299
Isobutyric	„	0·268
Chloracetic	„	4·300

* Cf. E. H. Rodd, “The Crystalline Form of Sulphonates,” ‘Roy. Soc. Proc.,’ A, vol. 89, p. 303 (1913).

Dichloroacetic acid		23.040
Trichloroacetic	„	68.200
Lactic	„	0.901
Trichlorolactic	„	6.900
Pyruvic	„	6.700
Oxalic	„	17.46
Malonic	„	2.87
Succinic	„	0.496
Tartaric	„	2.296
Malic	„	1.181
Citric	„	1.035

An explanation of the difference is to be found probably in two directions. Whatever tendency there may be in the sulphonic acids to undergo polymerisation, it appears probable from the behaviour of such acids in general that the complex molecule is easily broken down in presence of water and that the acid soon reaches a high degree of activity if not its maximum possible strength.

The depolymerisation of carboxylic acids, on the other hand, appears to take place, as a rule, with extreme slowness and to approach completion only at high dilutions—and the structure of the polymerised molecules is such apparently that they have little “strength” as acids.

In the second place, the sulphonic radicle appears to have an almost constant acidic value, whatever its associate may be. The carboxylic radicle, however, seems to vary greatly in acidic power and is presumably more “plastic” than the sulphonic radicle: it is difficult to account for the extraordinary difference in behaviour manifest between acetic acid and its chlorinated derivatives, for example, on any other assumption, though the introduction into acetic acid of chlorine in place of hydrogen may well render the molecules less prone to undergo polymerisation in aqueous solution, owing to the increased tendency of the fundamental molecules to combine with water rather than with each other—so that the difference between acetic and trichloroacetic acid may be due, in no small measure, to the fact that the former is present mainly in the polymerised inactive form whilst the trichlorinated acid is present in the form of simple molecules.

It is difficult to believe that the free carboxylic radicle, COOH , has an activity comparable with that of the SO_3H radicle in the sulphonic acids: the facts generally appear to be more in harmony with the view that it has a fluctuating value and that its intrinsic strength is largely a question of the nature of its associate.

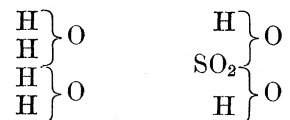
In view of the assumption that is often made that carbonic acid is hydroxyformic acid, it may be pointed out here that its extreme weakness is against this view: as it should be stronger than formic acid, if so constituted, especially as there is no reason to believe that it exists in solution in a polymerised form.*

The Constitution of Sulphuric Acid.

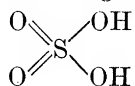
Taking into account the properties generally of the acid—particularly the fact that the “strength” of the acid-ethereal-sulphates and of the sulphonic radicle (SO_3H) in sulphonic acids is so considerable and not far removed from that of sulphuric acid itself—there is little to support the view that sulphuric acid is a dibasic acid in any proper sense of the term; there is much, however, to justify the conclusion that its primary behaviour is monacidic and, in fact, that of a very strong “monobasic” acid. Apparently, however, at high dilutions, it is capable of manifesting a second but quite different order of activity.

The symmetrical formula commonly attributed to sulphuric acid, $\text{SO}_4\text{H}_2 = \text{SO}_2(\text{OH})_2$, not only does not correspond with the behaviour of the compound even as an acid but it may be asserted that not a single interaction is known which renders the adoption of such a symbolic expression necessary.

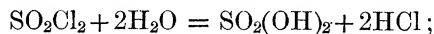
At the outset, sulphuric acid was formulated by Williamson, on the water type, as derived from two molecules of water—



in consequence of its presumed relationship to the two chlorides SO_3HCl and SO_2Cl_2 : when considerably later, mainly through Frankland's influence, resolved structural formulæ came into vogue, this formula became—



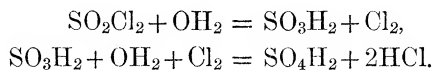
The formation of sulphuric acid from sulphuryl chloride, SO_2Cl_2 , is not necessarily a proof, however, that the acid contains two (OH) groups, as it may be equally well supposed either that the chloride is directly convertible into the acid, thus:—



or that it is primarily resolved into sulphurous acid and chlorine, which

* *Cp.* ‘Ber. deut. Chem. Ges.’ 1914, p. 945.

interact, *in statu nascendi*, giving rise to sulphuric acid and hydrogen chloride :—



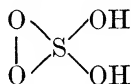
In like manner, the formation of the chloride SO_3HCl is not necessarily a proof of the presence of an OH group in the acid, as the primary action of phosphorus pentachloride may be merely to “dehydrate” the acid :—



Whilst there has been agreement as to the hydroxylic character of the acid, the general structure has been the subject of considerable argument—Kekulé, who consistently maintained the doctrine of constant valency and held that sulphur was a dyad, represented the acid by the formula :—



It has also been represented by the formula—



in which sulphur appears as a tetrad element. And that sulphur does sometimes function as a tetrad follows from the proof given by Pope and Peachey* that compounds of the type $(\text{R.R}_1\text{R}_2)\text{S.X}$ are optically active; but there is no satisfactory evidence that it ever has a higher valency, though it is often asserted that the hexad character of the element is established by the existence of a hexafluoride, SF_6 . The peculiar properties of this compound are better accounted for, however, by the assumption that the fluorine atoms form a closed system: the fluoride cannot well be used, therefore, as a proof of the valency of sulphur.

The discussion entered on a new stage when Barlow and Pope advanced the proposition that the “volume sphere of influence” (Valency-volume) of sulphur, like that of oxygen, is never more than about twice that of hydrogen.

Having formed the opinion that sulphuric acid is a monacidic compound like the sulphonic acids, we have been led to consider the problem of the structure of the sulphonic acids and of sulphuric acid with reference to the crystalline structure of the sulphonic compounds, from the point of view dealt with in the communication on this subject by Armstrong, Colgate and Rodd (*cp.* these ‘Proceedings,’ *seq.* pp. 111–173).

We shall base our arguments on the assumption that sulphur, like oxygen, whilst potentially a tetrad, usually functions as a dyad.

* ‘Trans. Chem. Soc.,’ vol. 77, p. 1072 (1900).

In the model of benzenesulphochloride shown in fig. 1, the sulphur atom is represented as connected with a (masked) carbon atom in the lower tier of atoms comprising the benzene unit and also as separately combined with two oxygen atoms which are not in direct connexion: the chlorine atom lies between these two oxygen atoms and presumably serves to connect them:

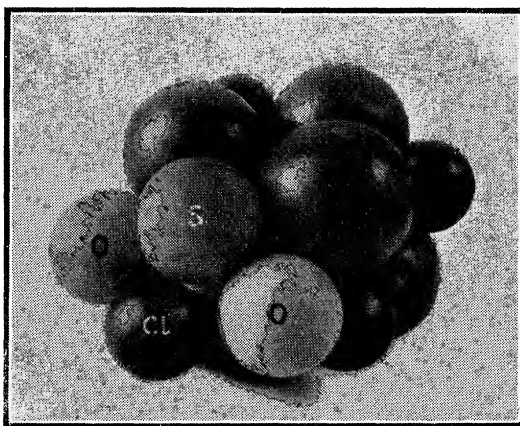


FIG. 1.—Model of Benzenesulphochloride.

but—assuming that the four affinities in oxygen and sulphur are directed tetrahedrally—there is no spare affinity of the sulphur atom in the direction of the chlorine atom: this, however, as well as the sulphur atom, has an affinity unsatisfied. In the solid compound, these spare affinities may operate in promoting the combination of the units in the crystalline substance; in solutions they may be in association with units of the solvent.

The unit of the sulphonic acid is obtained from that of the chloride by substituting the “triad” compound radicle OH for the triad simple radicle Cl.

The method of constructing an assemblage representing the crystalline structure of a compound substance introduced by Barlow and Pope consists in causing two or more units, each representing in composition and configuration one component of the compound, to interlock, the several component assemblages being intercalated homogeneously in such manner that the cavities formed in the one are occupied by the groups present in the others.

Conversely the structural units representing the several components of a compound molecule can be traced in and dissected out from the assemblage representing the crystalline structure of the substance. The important result to which we are permitted to call attention is that on applying their method to the sulphates, Messrs. Barlow and Pope have been led to formulate these salts crystallographically as compounds of the type $\text{SO}_3\cdot\text{OR}_2$, not as

compounds of the hydroxylic type, $\text{SO}_2(\text{OH})_2$: a return is thus suggested to the view originally introduced by Lavoisier and consistently advocated by Berzelius. Apart from the crystallographic evidence favouring this mode of treatment, the correctness of the view is also indicated by the existence of the well-defined hydrates $2\text{SO}_3\cdot\text{OH}_2$, $\text{SO}_3\cdot\text{OH}_2$, $\text{SO}_3\cdot 2\text{OH}_2$ and of stable salts such as $\text{Na}_2\text{S}_2\text{O}_7$, Pb_2SO_5 and Hg_3SO_6 , corresponding to them, as well as by the fact that the ordinary salts of telluric acid are derived from the hydrate $\text{TeO}_3\cdot 3\text{H}_2\text{O}$.*

The model shown in fig. 2 and in projection in fig. 3*a* embodies the conception referred to and appears to us to be a satisfactory expression of the chemical behaviour of the acid.

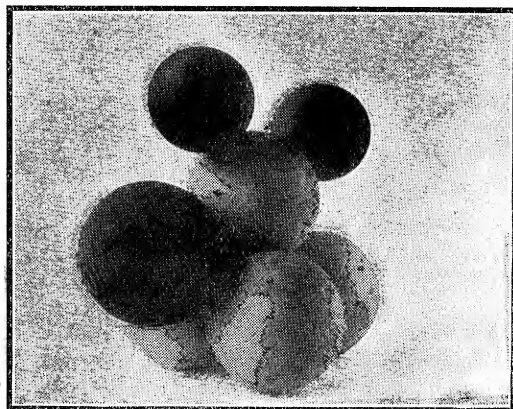


FIG. 2.—Model of Dihydrogen Sulphate (Sulphuric Acid), $\text{SO}_3\cdot\text{OH}_2$.

In the model, the sulphur atom exercises the function of a dyad: it may be supposed either that two affinities of the atom are latent or—as there is reason to believe that the acid is an “associated” substance—that they serve to maintain the connexion between two or more units such as that shown.

Two only of the oxygen atoms are in direct connection with the sulphur atom but a third atom serves to unite them, so that the complex SO_3 forms a closed system. In the “acid,” the two oxygen atoms adjoining the sulphur atom are further united by the radicle OH_2 , leaving each with an affinity “free” but in the plane below that in which the OH_2 group is situated.

The attachment of a second OH_2 to the same two oxygen atoms in this lower plane may be supposed to give rise to the monohydrate of sulphuric

* The crystalline hydrate $\text{SO}_4\text{H}_2\cdot 4\text{H}_2\text{O}$ is perhaps formed by the union of $3\text{H}_2\text{O}$ *en bloc* with the monohydrate $\text{SO}_4\text{H}_2\cdot\text{OH}_2$: in fact, the possibility that the complex hydrates are formed by the inclusion of one or other of the polyhydrones (these Studies, No. VI) in the crystalline structure is obviously one that must be taken into consideration in future discussions of the constitution of hydrates.

“acid”: or this second hydrate might be formed by the attachment of OH_2 to what may be termed the median oxygen atom of the SO_3 unit. It is equally conceivable that the first and second hydrates may be formed in the reverse order.

It is noteworthy that while the “fixation” of the first molecular proportion of hydrone by sulphuric anhydride involves the evolution of 21,320 units of heat, that of the second affords 6379 and that of the third only 3039 units: the additional amount of heat given out on continuing the dilution is eventually about equal to that evolved on first mixing the acid with two molecular proportions of water and the whole amount evolved on dissolving the “acid” (H_2SO_4) in water is less than that evolved on converting the anhydride into the acid.

A distinction of consequence is to be drawn between the manner in which the OH_2 radicles become attached to the anhydride: the first may be regarded as directly associated without alteration; the second—that which unites with the median oxygen atom—may be supposed to be “distributed” as it enters into combination, so that this oxygen atom is “hydrolated,” to use the term introduced by one of us in No. VI of these Studies.* The median oxygen atom, therefore, has specific properties and we are inclined to regard this as the “centre of activity” in the molecule of the acid: hence also perhaps the behaviour of the acid—*its essentially monacid character*. The properties of oil of vitriol are such as to favour the view that the compound H_2SO_4 is polymerised readily and that dilution is a process of depolymerisation. It is probable, in fact, that the gradual increase in the activity of the acid, as shown by the rise in molecular conductivity as dilution proceeds, is a consequence of the gradual “unmasking” of the sulphur atom and due to its more or less complete “hydrolation.”

The active units in a solution of the acid are presumably either of the type shown in fig. 3*b* or the correlate of this compound which is formed by the distribution of the acid molecule against the hydrone molecule: or it may be that in concentrated solutions two such units act together and that when the solution is diluted the complex is gradually resolved into “hydrolates” of the form shown in fig. 3*c*.

On such an assumption it is possible to understand the considerable increase in molecular electrical conductivity which attends the dilution of sulphuric acid, on account of which it is apparently to be ranked as a dibasic acid.†

* ‘Roy. Soc. Proc.,’ A, vol. 81, p. 80 (1908).

† If it be supposed that sulphuric acid is diacidic even in concentrated solutions, the equivalent strength of the acid will be but little more than half that of either nitric or

Two conclusions that are necessary if our view of the constitution of sulphuric acid be correct should be mentioned here. One is that the formation of anhydrous sulphates of the metals is to be regarded as an indirect process: not as the outcome of the direct displacement of one or both

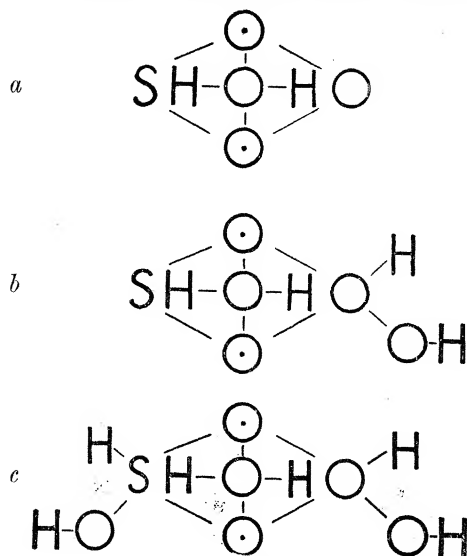


FIG. 3.

hydrogen atoms but as a process of isomeric change in which the metal passes into a final position of rest from the position it assumes in the hydrolated molecule at entry, the other is that the sulphonic acids are not directly derived from sulphuric acid but are compounds of a distinct type—a conclusion of some interest and importance in connexion with the superior strength of sulphuric acid in comparison with the monosulphonic acids.

In the formula we have suggested, the active “centre” in sulphuric acid is the third atom of oxygen by the addition of which the weakly acidic sulphur dioxide is converted into the intensely acidic sulphur trioxide; the cause of the great difference in behaviour of sulphuric in comparison with sulphurous acid is therefore brought to expression in the formula.

The views here put forward may be applied to other “acids,” especially to carbonic, silicic, phosphoric and arsenic acids. These probably are all to be regarded as compounds of the anhydrides with hydrone rather than as hydroxylic derivatives: though *polybasic*, they are all essentially *monacidic*, like sulphuric acid.

chlorhydric acid. Such a conclusion is altogether improbable in view of the properties of the compound; moreover, it must then be supposed that it is potentially tetracidic in weak solutions, to account for the increase in its molecular electrical conductivity on dilution.

The Nature of Acidity.

If the term acid is to be attached to the chemically active substance in an acid solution, it is not logical to speak either of the halhydrides or of compounds such as are represented by the formulæ NO_3H and SO_4H_2 as acids—the acid being the product formed in solution by the interaction of solvent and solute.

It is therefore of primary importance that we should seek an agreement as to the nature of the processes of dissolution and of “acidification.” The conception that the dissolved substance is directly dissociated into electrically charged ions, introduced by Clausius, which Arrhenius has done so much service by carrying to a logical issue, cannot be accepted in its original form, as it is impossible to admit that the solvent acts merely as a screen and that the separate ions are present and move about freely in the solution, being kept apart by the mere interposition of the neutral molecules of the solvent.

Moreover, it cannot well be supposed that the ions are torn asunder owing to the attractions exerted by the molecules of the solvent and that they move about separately in the liquid in a hydrated condition; such an assumption involves the conclusion that the influence of the charges by which, *ex hypothesi*, the ions are held together is overcome by superior force and this could only happen if the ions gave up their charges in combining with the solvent molecules; by so doing, however, they would necessarily lose the magic attribute which gives them the special properties they possess in the eyes of the dissociationist.

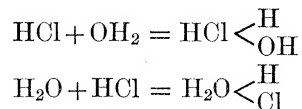
It is impossible, in fact, to grant more than potential freedom—superior attractive power—to the ions; this is secured by the hypothesis advocated by one of us from 1885 onwards and ultimately developed in 1908 (No. XI) into the view that the molecules of solvent and of solute are equally concerned and that the active “substance” is compounded of the two agents.

Every chemist is both taught and prepared to believe that ammonia and hydrogen chloride give rise to ammonium chloride $\left(\text{H}_3\text{N} < \begin{smallmatrix} \text{H} \\ \text{Cl} \end{smallmatrix}\right)$ and that ammonia and hydrone give rise to ammonium hydroxide $\left(\text{H}_3\text{N} < \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}\right)$: in other words, that hydrogen chloride and hydroxide both become divided up or dissociated at a nitrogen surface and that their radicles or “ions” combine separately with the nitrogen atom.

It is only necessary to extend the doctrine to the formation of acids, bases and “salts” generally.

To take the case of hydrogen chloride, if it be supposed that it becomes

active *as an acid* when dissolved in water because the reciprocal interactions take place which are pictured in the equations



the degree of "activation" will depend on the extent to which such changes are carried. In the case of a weak substance, like ammonia or "acetic acid," such changes take place presumably to a minimum extent; in the case of strong agents, such as hydrogen chloride and sulphate, they are at a maximum. The extent to which *relatively* the one or the other of the two reciprocal changes takes place must be supposed to be determined mainly by the relative concentration of the two substances.

No distinction can be drawn, from this point of view, between the concentrations of the "ions" of an acid—they are necessarily present in equivalent amounts. To speak of the effective acidity of an acid solution in terms of the concentration of the hydrogen ions, is to give an altogether misleading impression; and if, as we believe, acidity be a complex function, it can only be determined by some practical test: the result should be reported, therefore, in terms of an accepted practical standard, not in terms of a purely hypothetical interpretation.

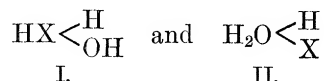
Enzymes, which simulate acids as hydrolytic agents and surpass them in activity, are beyond all question agents which act selectively: in virtue, it must be supposed, of specific qualities, not because they contribute "hydrogen ions": but there is no less reason to believe that acids act in virtue of their specific characters and as wholes than there is to believe that enzymes act specifically. The hypothesis that the characteristic activity of acids is due to the hydrogen ion and to this alone and the activity of alkalies, in like manner, to the hydroxyl ion—because the hydrogen and the hydroxyl ion respectively are common, the former to all acids, the latter to all alkalies—is one, in fact, which it is difficult to treat seriously. It is as improbable and as much in opposition to our general experience as is the primary hypothesis of the dissociationist school that the ions fall apart immediately a potential electrolyte is dissolved in water. Moreover that the addition of oxygen or the introduction of chlorine in place of hydrogen (in the well known case of trichloroacetic acid, for example), should make a compound a stronger acid by rendering it more prone to part with hydrogen is inconceivable.

Unfortunately, qualities are of no account in the eyes of the physical chemist of to-day. Hence it is that it has been customary of late years to regard hydrogen chloride and water as entirely unrelated substances and that

it has been seriously assumed that when the two are mixed together the molecules of the one remain almost all unchanged whilst those of the other are almost all dissociated into their ions. The chemist who takes facts generally into account cannot possibly admit that any such distinction exists.

In our opinion, the acidity of an acid is a function of the acid molecule as a whole—of its “ions” collectively and co-operatively—not of one of its parts taken singly or separately and apart from the other; in all cases, moreover, the presence of water (or rather of its fundamental molecule, hydrone) is essential to the formation of the acid proper.

The hypothesis we advocate is in accord with all the ordinary canons of the chemist's belief, inasmuch as it involves the assumption that the two necessary constituents of an acid electrolyte interact reciprocally and give rise to two compounds, thus—



so that both are “ionized,” not one of them only.

The proportions in which the two “reciprocals” are present will depend upon the concentration and, assuming that both play their part, the manner in which change takes place under their influence will depend both on the relative and on the absolute proportions in which they are present. If it be assumed that the oxonium compound (II) is present in major proportion in concentrated solutions of hydrogen chloride, for example, it follows that this is at least the more active agent in promoting hydrolytic change. On the other hand, the assumption that the chloride is “hydrolated” to the maximum extent in dilute solutions would serve to explain the fact that the molecular conductivity of the hydrogen chloride rises to a maximum as the solution is diluted.

From such a point of view, it is possible perhaps to explain the lack of agreement in the results given by the hydrolytic and electrolytic methods of contrasting acids. In the case of acids of the same degree of basicity, all have very nearly the same activity in sufficiently dilute solutions, judging from their molecular electrical conductivities: but they are found to differ very greatly in strength when their behaviour as hydrolytic agents is determined. If it be assumed that conductivity depends merely on the extent to which the molecules are brought into action owing to their arrangements in chains, without reference to the stability of or to the attractions existent within the chains that are formed, it is not difficult to understand that the behaviour of acids should be more nearly alike the more completely the molecules are brought into line and arranged in

conducting chains: but strength (in an acid) may be supposed to depend merely on the degree of affinity—the attractive power—which the acid radicle has for the hydrolyte: it may well be therefore that of the reciprocal forms present in the electrolyte that of the oxonium type is the essential agent in cases of hydrolytic change and that the compounds of this type formed from different acids differ more or less in strength. Conductivity, in other words, is less a measure of strength than of continuity of action—as in the case of a series of individuals passing buckets of water to put out a fire: everything depends on the formation of the “chain”: the individual units may be either weak or strong; provided they act together in unison and continue to pass the buckets along, they are effective agents, though the rate at which and the extent to which they are effective is necessarily limited by the degree of activity exercised by the weakest member of the series.

In an alkaline solution, there will be two positive ions present, hydrogen and the metal, in numbers equal in sum to the number of hydroxyl ions: in an acid solution, two negative ions, in numbers equal in sum to the hydrogen ions.

According to our view, both constituents of a solution play an active part: to the present day, the advocates of ionic dissociation think only of the solute as active. Consequently, by paying attention only to two ions—hydrogen and the one negative acid radicle, in the case of an acid—they have arrived at the illogical conclusion that the positive and negative ions convey the current in different proportions: had they taken into account the part played by both negative radicles (or in the case of alkalies, that played by the two positive radicles concerned), it would have been realised that no such difference exists and that a factor of extreme importance has been overlooked.

[My thanks are due to the Royal Society, to the Goldsmiths' Company and to the Leathersellers' Company for the assistance they have granted to me at various stages of the inquiry dealt with in this and the following communication: also to Dr. R. Messel, F.R.S., to whom I am particularly indebted, as he has ever been ready, during a long series of years, to promote my sulphonation studies.—H. E. A.]



FIG. 1.—Model of Benzenesulphochloride.

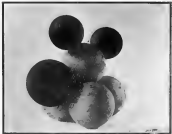


FIG. 2.—Model of Dihydrogen Sulphate (Sulphuric Acid), SO_4OH_2 .